

# Modelling sugar crystallization including morphology quantification

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## Abstract

An image analysis technique developed by the authors allows the quantification of the morphology of sugar crystals, namely its agglomeration degree. In this work, this technique is used to validate a model for sugar crystallisation in a laboratory batch crystalliser. The validation data includes the on-line measurements of the sugar contents in the solution and the system temperature. The distributions of the crystal population size and of the degree of agglomeration are used as final validation data. The model considers crystal growth, nucleation and agglomeration.

## 1 Introduction

Agglomeration in crystallising systems is one of the least understood crystallisation mechanisms. In part this is due to the lack of a direct measurement of this crystal property. Until now, only its effect on crystal size distribution was being taken into account in model development.

A technique previously developed by the authors (Faria et al., 2003) allows a direct measurement of the agglomeration degree of sucrose crystals.

In this work, a crystallisation model is developed in order to allow the simulation of this new property.

Finally, an example of experimental and simulated results, obtained in a fully instrumented laboratory crystalliser, are presented.

## 2 The model

The model used in this work is based on the model developed by Chorão (1995) to simulate an industrial batch sugar crystalliser.

In order to account for the nucleation, growth, growth rate dispersion and agglomeration phenomena, the crystal size population balance was discretised according to the technique proposed by Hounslow et al. (1988).

Next, a short summary of the main model equations is presented.

Equation 1 represents the discretised population size balance.

$$\left(\frac{dn_i}{dt}\right)_{\text{total}} = \left(\frac{dn_i}{dt}\right)_{\text{nuc}} + \left(\frac{dn_i}{dt}\right)_{\text{growth}} + \left(\frac{dn_i}{dt}\right)_{\text{aggl}} \quad (1)$$

The nucleation, growth and agglomeration expressions are presented in equations 2, 3 and 4, respectively.

$$\left(\frac{dn_1}{dt}\right)_{\text{nuc}} = B_0 \quad (2)$$

$$\left(\frac{dn_i}{dt}\right)_{\text{growth}} = 3.5 \frac{G}{L_i} \left(n_{i-1} - \frac{1}{r} n_i\right) + 3.2 \frac{D_g}{L_i^2} \left(n_{i-1} - \frac{1}{r^2} n_i\right) \quad (3)$$

$$\begin{aligned} \left(\frac{dn_i}{dt}\right)_{\text{aggl}} = & n_{i-1} \sum_{j=1}^{i-1} [2^{j-i+1} \beta_{i-1,j} n_j] + \frac{1}{2} \beta_{i-1,i-1} n_{i-1}^2 \\ & - n_i \sum_{j=1}^{i-1} [2^{j-i} \beta_{i,j} n_j] - n_i \sum_{j=i}^{N_{\text{disc}}} [\beta_{i,j} n_j] \end{aligned} \quad (4)$$

The kinetic expressions are presented in equations 5, 6, 7 and 8.

$$B_0 = \frac{K_b}{\rho_m} G^{b_1} \left(\frac{\rho_m}{\rho_c} \frac{m_c}{k_v}\right)^{b_2} \quad (5)$$

$$G = K_g \exp\left(\frac{-67400}{8.314(T_m + 273.15)}\right) \Delta C^{86.58\bar{L} + 1.1768\bar{L}^{0.54}} \quad (6)$$

$$D_g = 5 \times 10^{-5} G \text{ m}^2/\text{s} \quad (7)$$

$$\beta_{i,j} = K_{\text{ag}} \frac{(L_{\text{crit}} L_i L_j)^2}{(1/2 L_{\text{crit}}^3 + L_i^3)(1/2 L_{\text{crit}}^3 + L_j^3)} G \left(\frac{m_c}{k_v} \frac{\rho_m}{\rho_c}\right) \quad (8)$$

Mass balance is presented in equations 9 and 10.

$$\frac{dm_{\text{sac}}}{dt} = -\frac{dm_c}{dt} = J_{\text{cris}} \quad (9)$$

$$J_{\text{cris}} = \rho_c k_v \sum_{i=1}^{N_{\text{disc}}} \bar{L}_i^3 \left[ \left(\frac{dn_i}{dt}\right)_{\text{nuc}} + \left(\frac{dn_i}{dt}\right)_{\text{growth}} \right] \quad (10)$$

### 3 Agglomeration degree population balance

With the development of the image analysis technique, namely the measurement of the agglomeration degree (Faria et al., 2003), it becomes possible to take this information into account in model development and validation.

The model derives from the following set of conditions:

1. the agglomeration degree, quantified in the variable  $Ag$ , is a number that may take any value between 0 and 1;
2. the agglomeration degree increases with the increase of the complexity of the crystal;
3. all crystals with an agglomeration degree less than 0.25 are considered to be not agglomerated (simple crystals);
4. at any time, the agglomeration degree of a discretisation size class is the average of the agglomeration degrees of all crystals with a size corresponding to this class;
5. all crystals belonging to size class  $i$  are considered to have an agglomeration degree of  $Ag_i$  – the agglomeration degree of size class  $i$ ;
6. when a crystal grows from size class  $i - 1$  to class  $i$ , the agglomeration degree of this last one changes by introducing a new crystal with agglomeration degree  $Ag_{i-1}$ ;
7. the agglomeration degree of a new crystal ( $Ag_n$ ), resulting from the agglomeration of two original crystals is equal to the sum of the relative size weighted average of their agglomeration degree with a term corresponding to this agglomeration event;
8. when a new crystal is formed by agglomeration, the agglomeration degree of its size class changes with the introduction of a new crystal with agglomeration degree  $Ag_n$ .

Conditions 1, 2, 3 and 4 are a direct consequence of the image analysis technique previously developed and the following statistical treatment of the data. On the other hand, the discretised nature of the model establishes the conditions 5, 6 and 8.

In what concerns the 7th condition, it may be divided in two distinct parts, each one corresponding to one of the two terms of the sum – the weighted average of the agglomeration degrees and the increase in the agglomeration degree due to the agglomeration event itself.

The first part results from the criteria established to build the four classes of the agglomeration tree (Faria et al., 2003) – simple, small, medium or high agglomeration. Indeed, the resulting classification of an agglomeration between a large and a small crystal is practically independent of the agglomeration degree of the small crystal as the predominant shape is that of the larger crystal, no matter how agglomerated they may be.

As for the second term of the sum, it produces the increase in the agglomeration degree due to the agglomeration in course. The quantification of this increase must agree with the original classification tree and the equations derived to measure the agglomeration

degree from image analysis data. From these, the following qualitative observations may be derived and these shall be used in the development of the model equation:

- If two simple crystals of the same size agglomerate, the resulting crystal is classified as medium agglomerated (MA), that is with an agglomeration degree around 2/3;
- In order to produce a small agglomerated crystal (SA) from two simple crystals, one of the original crystals must be considerably smaller than the other. The agglomeration degree of an SA crystal should be close to 1/3;
- Very agglomerated crystals (VA) always result from agglomeration between crystals which were already classified as agglomerated. The agglomeration degree of a VA crystal is higher than 0.75;
- The resulting crystal of an agglomeration between an SA crystal with a considerably smaller one, should be classified as MA.

We now present, for the first time, equation 11. The agglomeration degree of a new crystal ( $Ag_{n_{i,j}}$ ), born from the agglomeration of two original crystals belonging to size classes  $i$  and  $j$ , with agglomeration degrees  $Ag_i$  and  $Ag_j$  and sizes  $\bar{L}_i$  and  $\bar{L}_j$ , is calculated by equation 11.

$$Ag_{n_{i,j}} = \frac{\bar{L}_i^2 Ag_i + \bar{L}_j^2 Ag_j}{\bar{L}_i^2 + \bar{L}_j^2} + \frac{1}{\left| \frac{\bar{L}_i - \bar{L}_j}{(\bar{L}_i + \bar{L}_j)/2} \right| + 1} \left( 1 - \frac{\bar{L}_i^2 Ag_i + \bar{L}_j^2 Ag_j}{\bar{L}_i^2 + \bar{L}_j^2} \right) \frac{2}{3} \quad (11)$$

In the first term of this equation, corresponding to the calculation of the mean value of the original agglomeration degrees, an area weighted average was employed. The reason behind this decision is that in the training stage of the image analysis technique (Faria et al., 2003), the technician visually classifies the agglomeration degree of the crystals based on a two dimensional projection of their shape.

The second term of the sum is made of the product of three factors. The third one, 2/3, represents the agglomeration degree resulting from the agglomeration of two identically sized, simple crystals.

As for the first factor, it accounts the effect of the difference in size between the two original crystals. If they have the same size, this first factor is neutral as it takes the value of 1. Otherwise, it approaches 1/3 with the increase in the size difference of the original crystals, lowering the agglomeration degree of the new crystal.

The function of the third factor is to lower the increase in the agglomeration degree of the new crystal as the the agglomeration degrees of the original crystals increases. This factor assures that the agglomeration degree of the new crystal is never higher than 1.

We are now in position to deduce the equation that shall calculate the evolution in time of the agglomeration degree of each size class. To do so we only need to do a balance to the number of crystals going in and out of a given size class and their respective agglomeration degree.

Let  $Ag_i(t_0)$  be the mean agglomeration degree of the crystals in size class  $i$  at the instant  $t_0$ . At  $t_0 + \Delta t$ , the agglomeration degree  $Ag_i(t_0 + \Delta t)$  represents the average of the agglomeration degrees of crystals in size class  $i$ , at  $t_0$ , crystals that enter this size class by growth or agglomeration and of crystals that leave this size class also by growth or agglomeration, during the time interval  $\Delta t$ . From a practical point of view,  $Ag_i(t_0 + \Delta t)$  is simply the quotient between the first order moment of the agglomeration degree distribution in each size class ( $\mu_{1,Ag_i}$ ) and the zeroth order moment ( $\mu_{0,Ag_i}$ ), at time  $t_0 + \Delta t$  (equation 12).

$$Ag_i(t_0 + \Delta t) = \mu_{1,Ag_i} / \mu_{0,Ag_i} \quad (12)$$

The zeroth order moment is simply calculated by adding the number of crystals of the size class at moment  $t_0$  with the respective crystal number variation between  $t_0$  and  $t_0 + \Delta t$  (equation 13).

$$\mu_{0,Ag_i}(t_0 + \Delta t) = n_i(t_0) + \int_{t_0}^{t_0 + \Delta t} \left( \frac{dn_i}{dt} \right)_{\text{total}} dt \quad (13)$$

In order to calculate the first order moment, we need to know not only how many crystals were in the size class and how many are going in or coming out of the interval, but also their respective agglomeration degree. This balance is present in the discretised population balance used to model the population size balance.

The positive terms account for crystals going into size class  $i$ . These must be multiplied by the agglomeration degree of the size class they originated from. In the case of growth, this is  $Ag_{i-1}$  and, in the case of agglomeration between a crystal from size class  $m$  with a crystal from size class  $n$ , it is  $Ag_{m,n}$ , calculated from equation 11.

The negative terms account for crystals going out of interval  $i$ . Taking into consideration the condition 5 of this model, these crystal have an agglomeration degree of  $Ag_i$ . The first order moment may then be calculated by equation 14.

$$\begin{aligned}
\mu_{1,Ag_i}(t_0 + \Delta t) = & n_i(t_0)Ag_i(t_0) + \int_{t_0}^{t_0+\Delta t} \left( 3.5 \frac{G}{L_i} + 3.2 \frac{D_g}{L_i^2} \right) n_{i-1}Ag_{i-1} dt \\
& - \int_{t_0}^{t_0+\Delta t} \left( 3.5 \frac{G}{r L_i} + 3.2 \frac{D_g}{r^2 L_i^2} \right) n_i Ag_i dt \\
& + \int_{t_0}^{t_0+\Delta t} n_{i-1} \sum_{j=1}^{i-1} [2^{j-i+1} \beta_{i-1,j} n_j Ag_{i-1,j}] dt \\
& + \int_{t_0}^{t_0+\Delta t} \frac{1}{2} \beta_{i-1,i-1} n_{i-1}^2 Ag_{i-1,i-1} dt \\
& - \int_{t_0}^{t_0+\Delta t} Ag_i n_i \sum_{j=1}^{i-1} [2^{j-i} \beta_{i,j} n_j] dt \\
& - \int_{t_0}^{t_0+\Delta t} Ag_i n_i \sum_{j=i}^{N_{\text{disc}}} [\beta_{i,j} n_j] dt
\end{aligned} \tag{14}$$

The agglomeration degree time balance equation may be calculated from the derivate definition, presented in equation 15.

$$\left. \frac{dAg_i}{dt} \right|_{t_0} = \lim_{\Delta t \rightarrow 0} \frac{Ag_i(t_0 + \Delta t) - Ag_i(t_0)}{\Delta t} \tag{15}$$

Combining equations 12, 13 and 14 and replacing  $Ag_i(t_0 + \Delta t)$  in equation 15, we get equation 16.

$$\begin{aligned}
\frac{dAg_i}{dt} = & \left[ \left( 3.5 \frac{G}{L_i} + 3.2 \frac{D_g}{L_i^2} \right) n_{i-1}Ag_{i-1} - \left( 3.5 \frac{G}{r L_i} + 3.2 \frac{D_g}{r^2 L_i^2} \right) n_i Ag_i \right. \\
& + n_{i-1} \sum_{j=1}^{i-1} (2^{j-i+1} \beta_{i-1,j} n_j Ag_{i-1,j}) + \frac{1}{2} \beta_{i-1,i-1} n_{i-1}^2 Ag_{i-1,i-1} \\
& \left. - Ag_i n_i \sum_{j=1}^{i-1} (2^{j-i} \beta_{i,j} n_j) - Ag_i n_i \sum_{j=i}^{N_{\text{disc}}} (\beta_{i,j} n_j) - \frac{dn_i}{dt} Ag_i \right] / n_i
\end{aligned} \tag{16}$$

The final form of the agglomeration degree balance equation is obtained by simplification of the previous equation where the  $dn_i/dt$  term is expanded according to the terms of the discretised crystal size distribution equation. The final result is presented in equation 17.

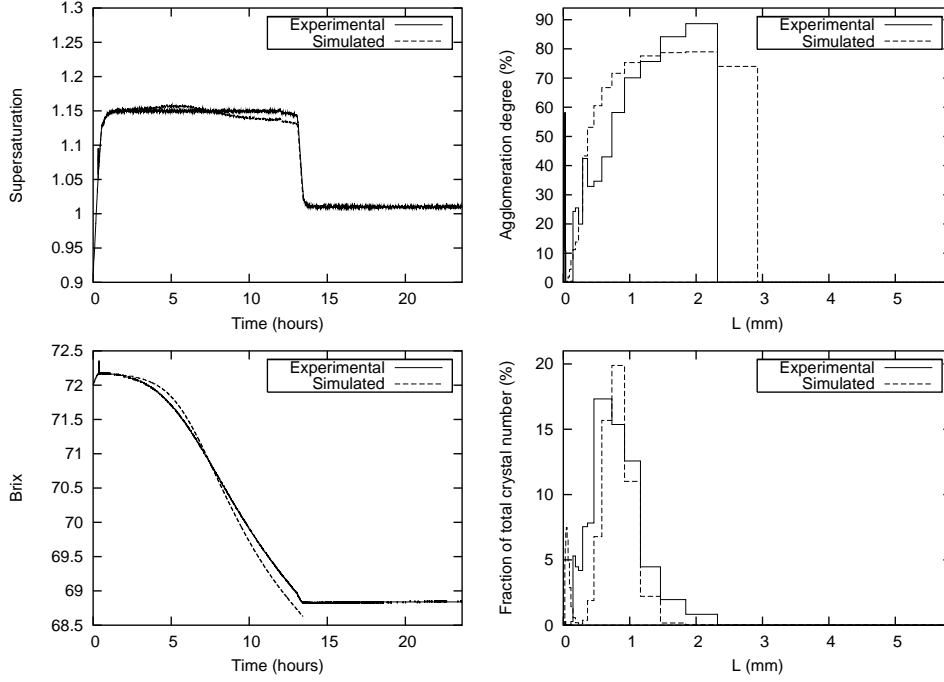


Figure 1: Experimental and simulated results

$$\begin{aligned}
\frac{dAg_i}{dt} = & \left[ \left( 3.5 \frac{G}{L_i} + 3.2 \frac{D_g}{L_i^2} \right) n_{i-1} (Ag_{i-1} - Ag_i) \right. \\
& + n_{i-1} \sum_{j=1}^{i-1} 2^{j-i+1} \beta_{i-1,j} n_j (Ag_{i-1,j} - Ag_i) \\
& \left. + \frac{1}{2} \beta_{i-1,i-1} n_{i-1}^2 (Ag_{i-1,i-1} - Ag_i) \right] / n_i
\end{aligned} \tag{17}$$

## 4 Simulation results

In figure 1, an example of a set of experimental and simulated results is presented.

This work presents, for the first time, an attempt to simulate the agglomeration degree distribution. It may be observed, that the model tends to predict an higher agglomeration degree for the smaller crystals and a lower agglomeration degree for the bigger ones. Also, the crystal size distribution tends predict less bigger crystals than the ones observed by the image analysis technique. These two observations are probably related and may be due to two different reasons. The most obvious one would be a failure in the agglomeration model which would fail to predict a higher agglomeration rate for bigger crystals. However, considering the experimental procedure used to filter and dry the crystals, it may happen

that the crystals are suffering from agglomeration during the drying phase which would result in the production of big, very agglomerated crystals.

## 5 Conclusion

Until now, agglomeration was only accounted for by its effect on the distribution of crystal sizes. It was necessary to have a priory knowledge of the growth rate, growth rate dispersion and nucleation kinetics to distinguish the agglomeration contribution to the shape of the crystal size distribution. The introduction of an independent and direct measurement of the agglomeration phenomena allows a quantification of this phenomena and consequently, its effect on the crystal size distribution.

Further improvements to the work presented may be aligned in two main vectors. On one hand, it is essential to follow the evolution of crystal properties as the experiments are carried out and not only the final result. It is known that crystal size and many other unaccounted for crystal properties have a strong effect on the agglomeration phenomena. During a batch crystallisation, the agglomeration kinetics should pass by drastically different values. Only if those values are measured as the experiment is conducted will it be possible to understand the mechanisms which result in the final agglomeration degree distribution.

On the other hand, the agglomeration degree balance equation is now being presented for the first time. The approximations it is based on are not always clear and further development of the model should improve the results obtained. However, it is pointless to put in a big effort in model development if this is not followed by an increase in the quality and quantity of experimental data available for model validation.

## References

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